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## CHEMICAL BIOLOGICAL CENTER

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ECBC-TR-804

### SELECTED PHYSICAL PROPERTIES OF 2-CHLOROETHYL-3-CHLOROPROPYL SULFIDE (CECPRS)

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<b>13. SUPPLEMENTARY NOTES</b>																				
<b>14. ABSTRACT</b> The vapor pressure, density, viscosity, surface tension, flash point, and melting point were determined for 2-chloroethyl-3-chloropropyl sulfide (CECPRS), which has been identified as a major impurity present in bis (2-chloroethyl sulfide) that had been stored in ton containers. This is the first time that all of these properties have been reported for CECPRS.																				
<b>15. SUBJECT TERMS</b> <table border="0" style="width:100%"><tr><td>CECPRS</td><td>2-chloroethyl-3-chloropropyl sulfide</td><td>Physical properties</td><td>Antoine equation</td><td>Viscosity</td></tr><tr><td>HD</td><td>Bis (2-chloroethyl sulfide)</td><td>Vapor pressure</td><td>Vapor saturation</td><td>Density</td></tr><tr><td>DSC</td><td>Differential scanning calorimetry</td><td>Surface tension</td><td>Melting point</td><td>Flash point</td></tr></table>						CECPRS	2-chloroethyl-3-chloropropyl sulfide	Physical properties	Antoine equation	Viscosity	HD	Bis (2-chloroethyl sulfide)	Vapor pressure	Vapor saturation	Density	DSC	Differential scanning calorimetry	Surface tension	Melting point	Flash point
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## **PREFACE**

The work described in this report was performed between August 2005 and September 2009. This work is documented in Laboratory Notebook Nos. 02-0091, 04-0073, 05-0107, and 06-0114.

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## SELECTED PHYSICAL PROPERTIES OF 2-CHLOROETHYL-3-CHLOROPROPYL SULFIDE (CECPRS)

### 1. INTRODUCTION

The compound 2-chloroethyl-3-chloropropyl sulfide (CECPRS) has been identified as a major impurity, present in bis (2-chloroethyl sulfide) (HD) that had been stored in ton containers.<sup>1</sup> The chemical structure of CECPRS is shown in Figure 1.

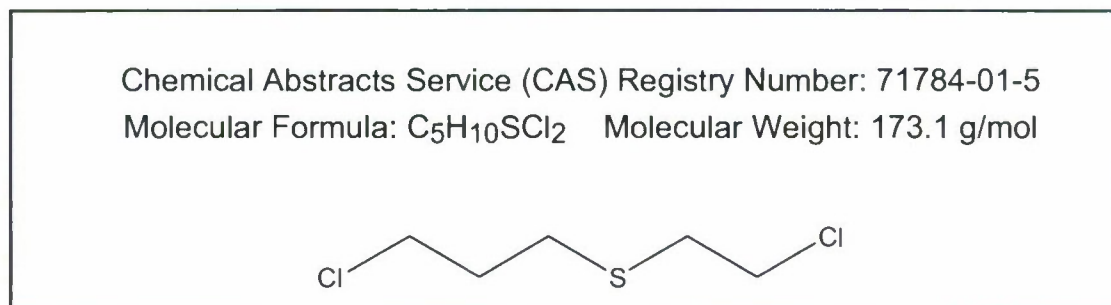


Figure 1. Chemical Structure of CECPRS

Modeling efforts, such as those underway in support of the Environmental Fate of Agents (Agent Fate) Program,<sup>2</sup> are affected by the presence of impurities in the agents of interest. In an effort to improve modeling efforts for HD, selected physical properties of CECPRS have been determined for the Agent Fate program and are reported herein.

The vapor pressure of CECPRS, which can be used to estimate the evaporation rate, is the physical property of most interest. Density, viscosity, surface tension, flash point, and melting point were also determined to provide a more complete characterization of this compound.

### 2. EXPERIMENTATION

#### 2.1 Materials

Table 1 provides origin and purity information for the three CECPRS samples used in this work. The samples were used without additional purification.

Table 1. CECPRS Sample Information

Property	Source	Lot Number	Purity
Vapor Pressure (Vapor Saturation)	ECBC	04-0046-56	99.1%
Vapor Pressure (Differential Scanning Calorimetry)	ECBC	48125-19,20,21	93.8%
Density, Viscosity, Surface Tension, Flash Point and Melting Point	Hestia Labs*	USAR04-04-1, PO 43899DC	99%

\*Hestia Laboratories, Inc., 16336 West Glendale Drive, New Berlin, WI.

## 2.2 Methods

### 2.2.1 Vapor Pressure

The vapor pressure of CECPRS was determined using two modified American Society for Testing and Materials International (ASTM) methods described in detail below (vapor saturation for the ambient temperature range and differential scanning calorimetry (DSC) for higher temperatures).

#### 2.2.1.1 DSC

Vapor pressure measurements were carried out using DSC in accordance with ASTM E 1782-03, *Standard Test Method for Determining Vapor Pressure by Thermal Analysis*.<sup>3</sup> For this work, a TA Instruments 910 Differential Scanning Calorimeter and 2200 Controller were used. Prior to sample measurements, the DSC was calibrated using ASTM E 967-03, *Standard Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers*.<sup>4</sup> The measurement consists of heating a small specimen of the test material in the DSC cell through the boiling point at a controlled rate, while the pressure (vacuum) on the cell is held constant. At the boiling point, the vaporized specimen escapes from the sample pan through a small orifice ("pinhole") in the lid. The energy associated with the transition from the liquid to vapor is recorded as a sharp boiling endotherm. The boiling point is taken at the intersection of tangents to the plot at the onset of boiling. The experimental pressure, measured with a mercury manometer, is the pressure in the cell as the specimen boils. This process is repeated with new specimens at different pressures.

The DSC method, using hermetic-type sealable pans with a pinhole  $\leq 125 \mu\text{m}$  in the lid, is recommended for use down to 5 kPa. At lower pressures, boiling endotherms broaden complicating accurate determination of extrapolated onset

temperatures from the intersection of tangents to the curve. Peak broadening reflects loss of equilibrium and self-pressurization as the rate of specimen vaporization inside the pan exceeds the rate at which molecules exit through the pinhole. Use of larger pinholes at lower pressures has been shown to restore peak sharpness consistent with a return to equilibrium boiling conditions.<sup>5</sup>

Subsequent unpublished quantitative studies with octanol have shown that although use of larger pinholes retains peak sharpness at lower pressures, method accuracy degrades.<sup>6</sup> Within the recommended ASTM pressure range down to 5 kPa, method uncertainty is  $\pm 1$  K. At 1330 Pa, the larger pinholes yielded boiling points within 2 K of literature values. This decreased accuracy remains an area of further study.

For applications where this increased uncertainty can be tolerated, such as in combination with data generated at even lower pressures by another method, DSC pinhole measurements below the recommended 5 kPa limit are appropriate.

#### 2.2.1.2 Vapor Saturation

A modified version of ASTM E 1194-07, *Standard Test Method for Vapor Pressure*<sup>7</sup> was used in this work. Vapor saturation measurements were conducted using the apparatus described previously,<sup>8</sup> including a Hewlett Packard Model 5890 Series II gas chromatograph (GC) equipped with a flame ionization detector (FID) as described in detail in an earlier report from our laboratory.<sup>9</sup> The glass saturator used in this effort was custom designed at the U.S. Army Edgewood Chemical Biological Center (ECBC). A schematic of the ambient temperature vapor pressure system is shown in Figure 2.

The equipment and procedures used to generate the saturated vapor stream for CECPRS are identical to those used earlier<sup>6, 8-13</sup> to measure ambient temperature vapor pressure data in our laboratory and will be summarized here. A CECPRS saturated vapor stream was generated at a known temperature using the saturator cell. CECPRS was collected in a saturated nitrogen stream at a controlled mass flow rate over a known time, concentrated, and the mass quantified by GC-FID analysis. This step enables vapor pressure measurements for low-volatility materials in the presence of high-volatility impurities, which was not a major problem in the present work.



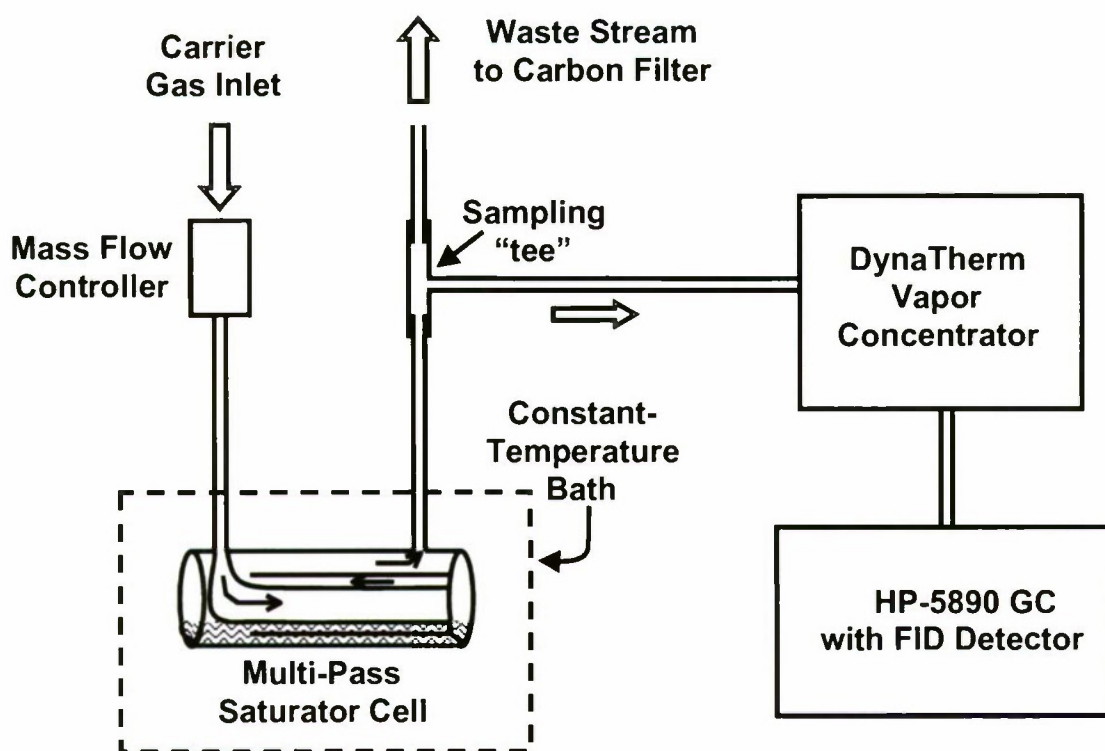


Figure 2. Schematic of Vapor Saturation Data Acquisition System

Saturated vapor streams were generated by flowing dry nitrogen carrier gas at 25 standard cubic centimeters per minute (sccm) through the saturator containing liquid CECPRS. In this work, the saturator was loaded with 5 g of liquid CECPRS, which was analyzed by GC using a thermal conductivity detector (TCD) before and after vapor pressure data were measured. Both analyses indicated 99.1 area % purity with no change in composition after 2 weeks of vapor pressure measurements with the major impurity remaining at 0.6% by GC-TCD throughout.

The temperature of the saturator was controlled by immersing it in a water-ethylene glycol bath. Using a calibrated thermometer, the temperature of the bath was measured to within 0.1 °C. Ambient pressure was measured periodically during each run using a Nova Model mercury barometer (Princo Instruments Incorporated, Southampton, PA). All barometer readings were corrected for temperature and latitude according to the manufacturer's directions. These readings were used in the vapor pressure calculation as described previously.<sup>8</sup> No corrections were included for the pressure drop between the sampling location and ambient. This correction is expected to be minimal because the flow stream was open to the atmosphere and there were no flow restrictions.

The saturator effluent was sampled as shown in Figure 2 by drawing 10 sccm to a modified ACEM Model 900 (Dynatherm Analytical Instruments, Inc., Kelton, PA) Tenax TA adsorbent (Tenax) concentrator collection tube maintained at 40 °C for between 2 and 60 min. The total volume of nitrogen carrier containing saturated CECPRS vapor ranged from 20 to 600 sccm. After sample collection, the Tenax collection tube was rapidly heated to 275 °C under a flow rate of 20 sccm using ultra high purity (UHP) grade nitrogen for 5 min and transferred to the ACEM 900 Tenax TA focusing trap maintained at 40 °C. Transfer continued for one additional minute to allow the 10-mm o.d. Tenax collection tube to cool. Then, the focusing trap was rapidly heated to 300 °C under a flow rate of 8.0 sccm UHP grade nitrogen for 5 min to effect sample transfer to the gas chromatographic column. The 15-m x 0.53-mm i.d. fused silica GC column (Restek Corporation, Bellefonte, PA), with a 1.0  $\mu\text{m}$  RT<sub>X</sub>-1 (polydimethylsiloxane) stationary phase, was maintained at 40 °C for 2 min following sample introduction, then heated at a rate of 10 °C/min to 220 °C for a GC run time of 20 min per sample.

An FID was used as the detection system for the saturator work. Nitrogen was used as the GC carrier gas at a flow rate of 8.0 cm<sup>3</sup>/min and as detector make-up gas at a flow rate of 22.0 cm<sup>3</sup>/min. Combustion gases were air at 400 cm<sup>3</sup>/min and hydrogen at 30 cm<sup>3</sup>/min.

Using the instrumentation and operating conditions described, CECPRS eluted at 10.1 min, which corresponded to a GC column temperature of 121 °C. Saturator GC vapor analyses revealed a relatively high purity sample with four minor impurities, all eluting before CECPRS on the non-polar, boiling point column. No new peaks were observed during the course of these measurements.

Calibration of the ACEM 900, HP 5890 FID system was accomplished by preparing a calibration standard solution by adding an accurately measured volume of CECPRS analyte to the hexane solvent and injecting known volumes of the resulting solution into the analytical stream. Ten microliters of neat CECPRS (99 mol % pure, sampled from the saturator) was added to about 7 mL of hexane (HPLC Grade, Burdick & Jackson, Muskegon, MI) using two aliquots from a 5- $\mu\text{L}$  Drummond Model 105 Digital Microdispenser (Drummond Scientific Company, Broomall, PA), then diluting to 10.0 mL with hexane. Converting this volume of CECPRS to mass using the liquid density at room temperature (1.21666 mg/ $\mu\text{L}$  at 25.1 °C) and correcting for CECPRS purity (99.1%) resulted in a solution with a concentration of 1.2057  $\mu\text{g}$  CECPRS/ $\mu\text{L}$  hexane. Precisely controlled masses were correlated to the resulting GC peak areas.

All calibrations were performed during the same day that the standard was prepared and bracketed the range of the measured vapor pressure data. The ACEM 900–5890 FID system was calibrated by making 1 to 5  $\mu\text{L}$  injections of the CECPRS standard into the distal end of the heated (100 °C) 1/16-in. o.d., 0.040-in. i.d. Sulfinert<sup>®</sup> tubing, which was supplied with dry nitrogen carrier gas at a flow rate of 10 sccm. ACEM 900 and GC operating parameters were identical to those used for experimental data acquisition with one exception. The ACEM 900 external sampling time for

calibration data was always maintained at 15 min to allow sufficient time for CECPRS transfer to the Tenax sampling tube. The resulting calibration curve is shown in Figure 3 and was generated by plotting FID area counts versus mass of CECPRS injected for the standard calibration runs. Equation 1 describes the calibration data set most accurately given the constraint that the calibration curve goes through the origin.

$$Y = mx \quad (1)$$

where

$$y = \text{GC-FID area (} 10^6 \text{ area counts)}$$

$$x = \text{analyte mass injected (}\mu\text{g)}$$

$$m = 2.3309$$

Calculation of vapor pressure from the indicated CECPRS mass associated with the measured FID area at each vapor pressure experimental temperature was performed as before.<sup>8</sup>

Vapor pressure values are inferred from the measured data using Equation 2, as described elsewhere<sup>8</sup> and using the sample purity to correct the indicated vapor pressure by dividing by the CECPRS mole fraction (0.99) in accordance with Raoult's Law. This calculation assumes Ideal Gas Law behavior.

$$VP_{\text{CECPRS}} = P_{\text{ambient}} \cdot n_{\text{CECPRS}} / (n_{\text{CECPRS}} + n_{\text{carrier}}) \quad (2)$$

where

$$VP_{\text{CECPRS}} = \text{vapor pressure of CECPRS calculated from measured data}$$

$$P_{\text{ambient}} = \text{ambient atmospheric pressure}$$

$$n_{\text{CECPRS}} = \text{number of moles of CECPRS, measured by GC-FID}$$

$$n_{\text{carrier}} = \text{number of moles of nitrogen carrier}$$



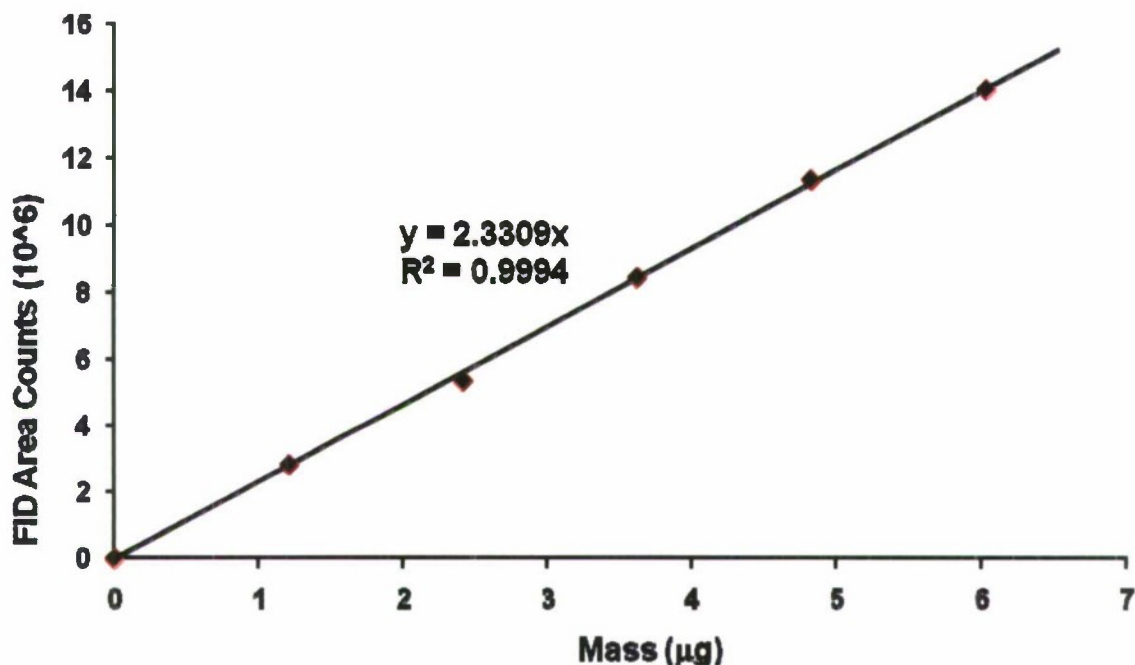


Figure 3. FID Calibration Curve and Analytical Equation for CECPRS

#### 2.2.2 Density

Liquid density was determined at 25, 35, and 50 °C in accordance with ASTM D 4052-96 (Reapproved 2002), *Standard Test Method for Density and Relative Density of Liquids by Digital Density Meter*<sup>14</sup> using an Anton Paar Model DMA 58 Digital Density Meter. This measurement is based on the change in frequency of an oscillating U-tube due to the presence of the test sample. Prior to sample measurements, the instrument was calibrated using air and distilled water at the experimental temperature. Proper instrument operation was validated by comparison to the National Institute of Standards and Technology (NIST) standard, toluene.

#### 2.2.3 Viscosity

Viscosity was determined at 25, 35, and 50 °C in accordance with ASTM D 445-09, *Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity)*<sup>15</sup> using a Cannon-Manning semi-micro viscometer and Cannon CT-1000 constant temperature bath. This measurement determines the flow rate of a liquid under gravity through a calibrated glass capillary viscometer. The viscometer used for this work was calibrated by the manufacturer.



#### 2.2.4 Surface Tension

Surface tension measurements were conducted at 25 °C using a KRUSS K12 Tensiometer with an external Lauda RM-6 circulating bath in accordance with Analytical Chemistry Method 069: *Determination of the Surface Tension of Liquids Using the Wilhelmy Plate Method (Appendix)*. This is a force measurement in which the normal force acting on the liquid surface, allows the liquid to conform to its smallest surface area. For this work, a small rectangular glass plate is lowered parallel to the liquid surface. The liquid is then raised until it just touches the bottom edge of the plate. Force on the plate increases due to wetting of the liquid against the plate. If the contact angle between the liquid and the plate is zero due to perfect wetting, then the surface tension is determined.<sup>16</sup> Proper operation of the tensiometer was validated using diethyl oxalate.

#### 2.2.5 Flash Point

Flash point was determined in accordance with ASTM D 6450-05, *Standard Test Method for Flash Point by Continuously Closed Cup (CCCFP) Tester*<sup>17</sup> using the Grabner FLPB Miniflash Tester. Prior to sample measurements, the instrument was validated for proper operation using n-dodecane.

Flash point is defined as the lowest temperature at which the vapor above the liquid specimen ignites when an ignition source (test flame) is applied. There are different ways in which this property can be determined.

The method used for this work, ASTM D 6450, defines the occurrence of a flash as the temperature at which the hot flame of the ignited vapor causes an instantaneous pressure increase ( $\Delta p$ ) of at least 20 kPa.<sup>17</sup> The Miniflash tester; however, defines a flash as the temperature at which the pressure exceeds a set threshold (default threshold = 20 kPa).<sup>18</sup> This condition is inconsistent with the ASTM  $\Delta p \geq 20$  kPa requirement. For example, if a sample has a baseline pressure higher than zero, the sample may exceed the 20 kPa threshold without producing a  $\Delta p \geq 20$  kPa. In order to address this concern, the threshold pressure was set to 50 kPa so that data could be collected over a wider pressure range for determination of a flash consistent with the ASTM requirements.

Flash point measurements using the continuously closed cup method normally provide stable pressure readings up to the point of the flash, which is denoted by a sharp, well-defined pressure increase when testing flammable, high purity samples. This is illustrated by the pressure profile for a 99.5 mol % pure sample of n-dodecane,<sup>17</sup> shown in Figure 4, which has a reported flash point of 79 °C (continuously-closed cup).

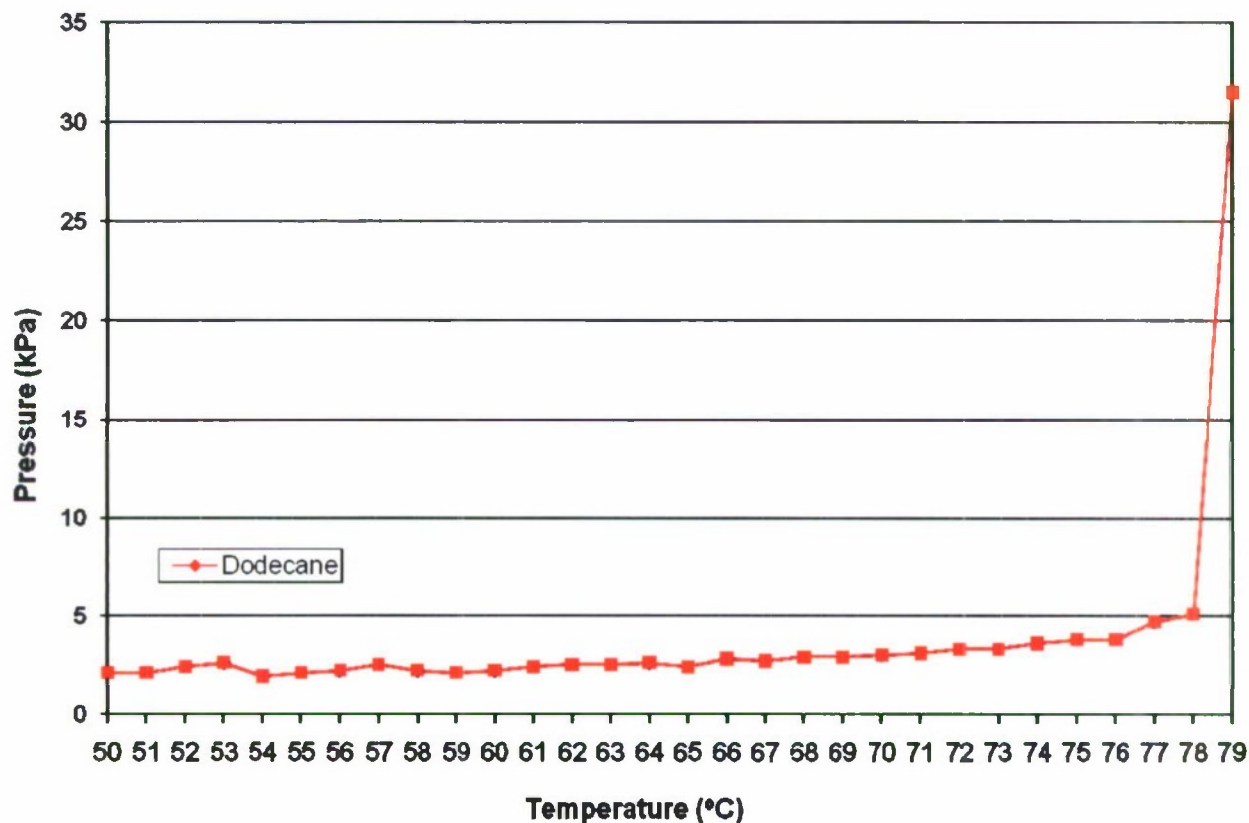


Figure 4. Flash Point Pressure Profile of n-Dodecane

#### 2.2.6 Melting Point

Melting point was determined in accordance ASTM E 794-06, *Standard Test Method for Melting and Crystallization Temperatures by Thermal Analysis*<sup>19</sup> using a TA Instruments 910 DSC with 2200 Controller. Prior to sample measurements, the DSC was calibrated with indium using ASTM E967-03, *Standard Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers*.<sup>4</sup>

### 3. RESULTS and DISCUSSION

#### 3.1 Vapor Pressure

Ambient temperature vapor saturation vapor pressure experiments were conducted from -20.0 to 20.0 °C with measured data obtained ranging from 0.0404 to 2.85 Pa. Each of the five saturator-determined vapor pressure data points

is actually the average of between 5 and 15 separate measurements taken after the data acquisition system had stabilized at each set of experimental conditions. One experiment was performed at a saturator flow rate of 50 sccm. The measured vapor pressure of CECPRS did not change with saturator flow rate, confirming that vapor-liquid equilibrium had been achieved at both flow rates.

DSC measurements were completed from 11 torr (1.47 kPa) to atmospheric pressure, corresponding to reduced boiling points from 118.0 to 234.0 °C. Thirteen clean, sharp boiling endotherms were measured between 11 and 300 torr (1.47 to 40.0 kPa), corresponding to 118.0 to 204.7 °C. At atmospheric pressure the boiling endotherms around 234 °C were erratic, consistent with decomposition. The calculated normal boiling point is 237.4 °C.

The experimental vapor pressure results from the two complementary techniques, DSC and vapor saturation, were combined into one data set and are listed in Table 2. This combined data set was then fitted to the Antoine equation<sup>20</sup> by minimizing the sum of the absolute percentage differences between measured and calculated values shown in Table 2. The Antoine constants with the corresponding version of the Antoine equation are listed in Table 3 with units of temperature in Kelvin and pressure in Pascal, as well as temperature in Celsius and pressure in torr.

The low percent differences between the measured and calculated values reflect the precision of this data set over the entire experimental range. This suggests excellent agreement between the two data sets and provides increased confidence in the accuracy of the data and supports the use of complementary methodologies to reduce the uncertainty in either data set alone.

Equations 3 and 4 were used to calculate the heat of vaporization and volatility,<sup>21</sup> respectively, as a function of temperature. Volatility is used extensively by the toxicology community, especially in reference to inhalation hazard determination.

The calculated vapor pressure, volatility, and heat of vaporization at selected temperatures within the range of measured data are given in Table 4. A plot of the experimental DSC and saturator data, as well as the calculated Antoine correlation, is shown in Figure 5. The normal boiling point calculated for CECPRS based on the present data is 237.4 °C (510.5 K); however, it should be noted that the DSC measurements completed at atmospheric pressure showed evidence of decomposition. A plot of the CECPRS combined data set Antoine fit is compared to that of HD<sup>11, 22</sup> in Figure 6. The change in slope in the HD fit indicates the change in physical state at 14.45 °C, which is the melting point.<sup>23</sup>



Table 2. Experimental DSC and Vapor Saturation Vapor Pressure Data for CECPRS

Temperature		P <sub>measured</sub>		P <sub>calculated</sub>		Difference* %
°C	K	Torr	Pa	Torr	Pa	
Vapor Saturation						
-20.0	253.15	3.030 x 10 <sup>-4</sup>	4.040 x 10 <sup>-2</sup>	2.976 x 10 <sup>-4</sup>	3.968 x 10 <sup>-2</sup>	1.82
-10.0	263.15	9.923 x 10 <sup>-4</sup>	1.323 x 10 <sup>-1</sup>	1.001 x 10 <sup>-3</sup>	1.335 x 10 <sup>-1</sup>	-0.90
0.0	273.15	3.042 x 10 <sup>-3</sup>	4.056 x 10 <sup>-1</sup>	3.034 x 10 <sup>-3</sup>	4.045 x 10 <sup>-1</sup>	0.28
10.0	283.15	8.383 x 10 <sup>-3</sup>	1.118 x 10 <sup>0</sup>	8.385 x 10 <sup>-3</sup>	1.118 x 10 <sup>0</sup>	-0.02
20.0	293.15	2.138 x 10 <sup>-2</sup>	2.850 x 10 <sup>0</sup>	2.138 x 10 <sup>-2</sup>	2.850 x 10 <sup>0</sup>	-0.01
DSC						
117.99	391.14	1.140 x 10 <sup>1</sup>	1.520 x 10 <sup>3</sup>	1.208 x 10 <sup>1</sup>	1.611 x 10 <sup>3</sup>	-5.64
122.33	395.48	1.430 x 10 <sup>1</sup>	1.907 x 10 <sup>3</sup>	1.475 x 10 <sup>1</sup>	1.966 x 10 <sup>3</sup>	-3.05
125.61	398.76	1.720 x 10 <sup>1</sup>	2.293 x 10 <sup>3</sup>	1.710 x 10 <sup>1</sup>	2.279 x 10 <sup>3</sup>	0.61
129.28	402.43	2.010 x 10 <sup>1</sup>	2.680 x 10 <sup>3</sup>	2.010 x 10 <sup>1</sup>	2.680 x 10 <sup>3</sup>	0.00
137.05	410.20	2.815 x 10 <sup>1</sup>	3.753 x 10 <sup>3</sup>	2.802 x 10 <sup>1</sup>	3.736 x 10 <sup>3</sup>	0.46
144.35	417.50	3.810 x 10 <sup>1</sup>	5.080 x 10 <sup>3</sup>	3.781 x 10 <sup>1</sup>	5.041 x 10 <sup>3</sup>	0.77
151.14	424.29	5.005 x 10 <sup>1</sup>	6.673 x 10 <sup>3</sup>	4.945 x 10 <sup>1</sup>	6.592 x 10 <sup>3</sup>	1.22
158.01	431.16	6.450 x 10 <sup>1</sup>	8.599 x 10 <sup>3</sup>	6.426 x 10 <sup>1</sup>	8.567 x 10 <sup>3</sup>	0.37
162.99	436.14	8.080 x 10 <sup>1</sup>	1.077 x 10 <sup>4</sup>	7.726 x 10 <sup>1</sup>	1.030 x 10 <sup>4</sup>	4.58
170.35	443.50	1.006 x 10 <sup>2</sup>	1.341 x 10 <sup>4</sup>	1.006 x 10 <sup>2</sup>	1.341 x 10 <sup>4</sup>	0.00
183.77	456.92	1.505 x 10 <sup>2</sup>	2.007 x 10 <sup>4</sup>	1.589 x 10 <sup>2</sup>	2.119 x 10 <sup>4</sup>	-5.29
191.25	464.40	2.000 x 10 <sup>2</sup>	2.666 x 10 <sup>4</sup>	2.025 x 10 <sup>2</sup>	2.699 x 10 <sup>4</sup>	-1.21
204.67	477.82	3.008 x 10 <sup>2</sup>	4.010 x 10 <sup>4</sup>	3.062 x 10 <sup>2</sup>	4.082 x 10 <sup>4</sup>	-1.77

\*[(measured-calculated)/calculated]\*100

Table 3. Antoine Coefficients for CECPRS

$\ln(P_{Pa}) = a - b/(c+T_K)$		
a	b	c
23.652	5686.0	-41.609
Temperature range: 253.2 to 477.8 K (-20.0 to 204.7 °C)		
$\log(P_{torr}) = A - B/(C+t_C)$		
A	B	C
8.1470	2469.4	231.54
Temperature range: 253.2 to 477.8 K (-20.0 to 204.7 °C)		

Enthalpy of Vaporization:

$$\Delta H_{\text{vap}} = RbT^2/(c + T)^2 \quad (3)$$

where

$\Delta H_{\text{vap}}$  = enthalpy of vaporization (kcal/mol)

R = gas constant [8.314 Joule/(K mol)]

b,c = Antoine constants

T = Temperature (K)

Volatility Equation:

$$V = PM/RT \quad (4)$$

where

V = Volatility (mg/m<sup>3</sup>)

P = Vapor Pressure (Pa)

M = Molecular mass (g/mol)

R = Gas constant [8.314 Joule/(K mol)]

T = Temperature (K)

Table 4. Calculated Properties for CECPRS at Selected Temperatures

Temperature (°C)	Vapor Pressure		Volatility (mg/m <sup>3</sup> )	Heat of Vaporization (kcal/mol)
	Torr	Pa		
-20	2.98 x 10 <sup>-4</sup>	3.97 x 10 <sup>-2</sup>	3.26 x 10 <sup>0</sup>	1.62 x 10 <sup>1</sup>
0	3.03 x 10 <sup>-3</sup>	4.05 x 10 <sup>-1</sup>	3.08 x 10 <sup>1</sup>	1.57 x 10 <sup>1</sup>
25	3.32 x 10 <sup>-2</sup>	4.43 x 10 <sup>0</sup>	3.09 x 10 <sup>2</sup>	1.53 x 10 <sup>1</sup>
50	2.38 x 10 <sup>-1</sup>	3.17 x 10 <sup>1</sup>	2.04 x 10 <sup>3</sup>	1.49 x 10 <sup>1</sup>
100	5.00 x 10 <sup>0</sup>	6.66 x 10 <sup>2</sup>	3.72 x 10 <sup>4</sup>	1.43 x 10 <sup>1</sup>
200	2.66 x 10 <sup>2</sup>	3.55 x 10 <sup>4</sup>	1.56 x 10 <sup>6</sup>	1.36 x 10 <sup>1</sup>

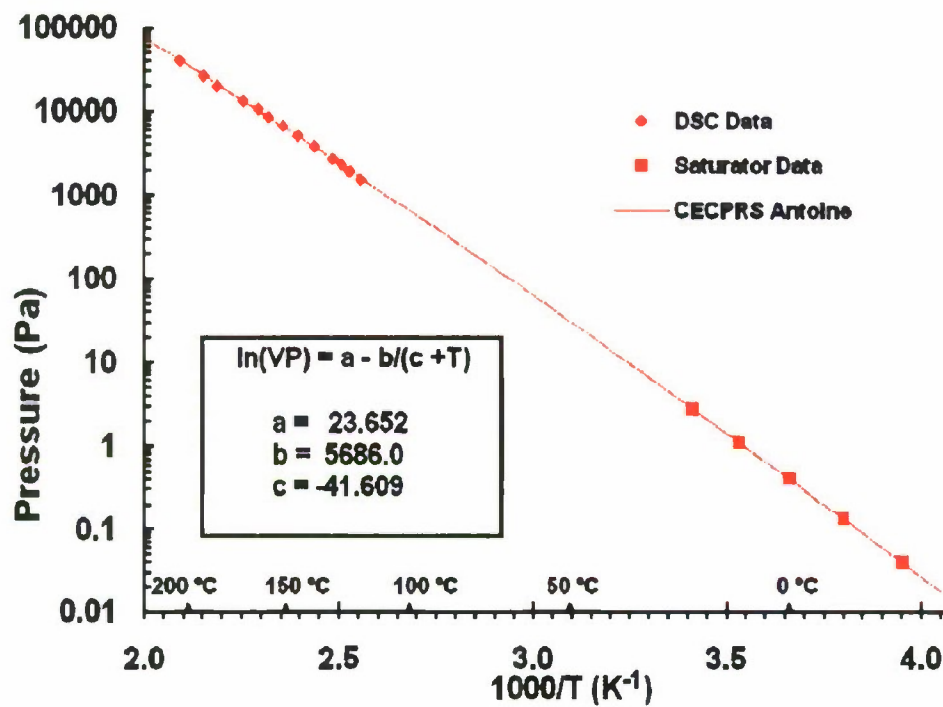


Figure 5. Experimental Vapor Pressure Data and Antoine Correlation for CECPRS

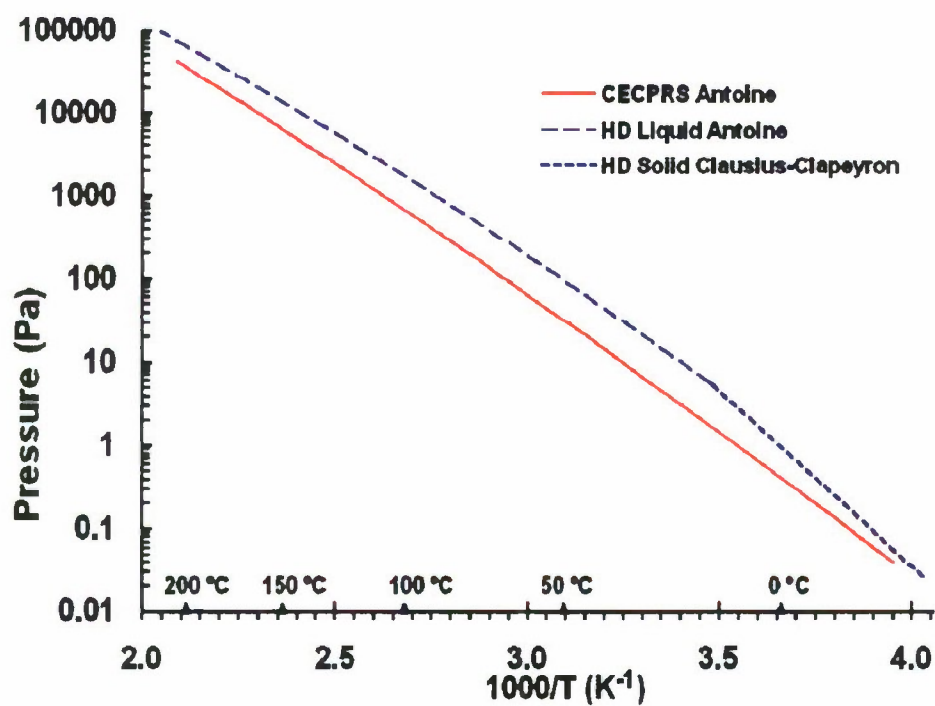


Figure 6. CECPRS Combined Antoine Correlation Compared to Liquid and Solid HD

### 3.2 Density

The experimental density data for CECPRS is provided in Table 5. This data, and the calculated linear fit are plotted together in Figure 7.

Table 5. Liquid Density of CECPRS

Temperature (°C)	Density* (g/mL)		Difference** %
	Measured	Calculated	
25.0	1.21679	1.21676	0.002
35.0	1.20662	1.20666	-0.004
50.0	1.19153	1.19151	0.001

\*The uncertainty of each measurement is  $\leq 0.00014$  g/mL.

\*\* $[(\text{measured}-\text{calculated})/\text{calculated}]*100$

Density Equation:

$$d = a + bt \quad (5)$$

where

d = density (g/mL)

a = 1.24202

b =  $-1.0101 \times 10^{-3}$

t = temperature (°C)

Experimental range: 25 – 50 °C

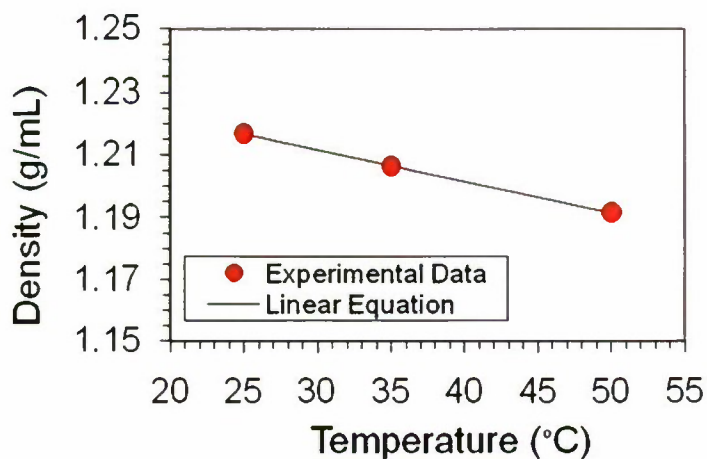


Figure 7. Liquid Density of CECPRS



A density value of 1.22635 g/mL at 20 °C for CECPRS was found in the literature.<sup>24</sup> Density measurements at ECBC were not conducted at 20 °C, however, the value calculated from eq 5 is in good agreement (-0.2 %) with the literature value. No experimental details were provided with the literature value, so this comparison should be used for informational purposes only.

### 3.3 Viscosity

The experimental viscosity results are listed in Table 6 and plotted in Figure 8 with the Antoine fit that was derived from eq 6.

Table 6: Viscosity of CECPRS

Temperature (°C)	Viscosity (cSt)			Difference** %
	Measured	Measured Mean*	Calculated	
25.0	3.2844	3.284	3.28441	-0.001
25.0	3.2858		3.28441	0.042
25.0	3.2811		3.28441	-0.101
35.0	2.6332	2.634	2.63344	-0.010
35.0	2.6337		2.63344	0.011
35.0	2.6335		2.63344	0.001
50.0	1.9691	1.969	1.96920	-0.007
50.0	1.9693		1.96920	0.007
50.0	1.9692		1.96920	-0.002

\*The uncertainty of each measurement is  $\leq 0.002$  cSt.

\*\* $[(\text{measured}-\text{calculated})/\text{calculated}]*100$

Viscosity (Antoine) Equation<sup>20</sup>:

$$\text{Log } \eta = A - B/(C + t) \quad (6)$$

where

$\eta$  = viscosity, cSt (centistokes)

t = temperature, °C

A = -1.29308

B = -323.225

C = 153.623

Experimental range: 25 to 50 °C

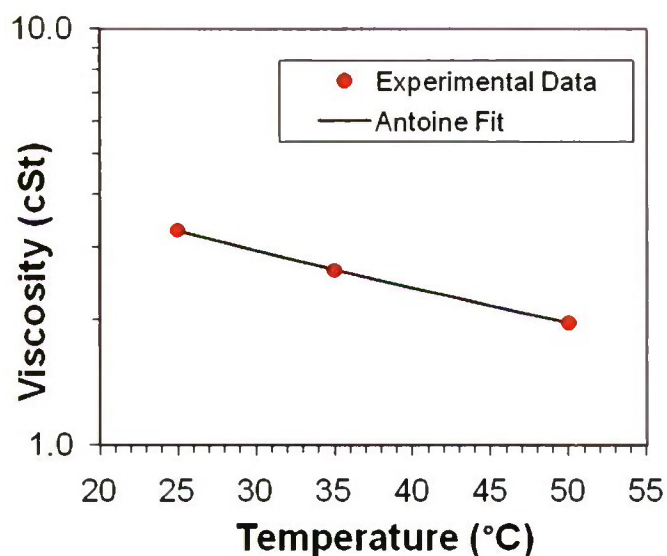


Figure 8. Viscosity of CECPRS

### 3.4 Surface Tension

Experimental surface tension data listed in Table 7 represents the mean of ten measurements.

Table 7. Surface Tension of CECPRS

Temperature (°C)	Surface Tension (dynes/cm)
25.0	41.20*

\*Standard Deviation = 0.04

### 3.5 Flash Point

CECPRS flash point measurements were run in triplicate and provided sharp, well-defined pressure increases. The average flash point by continuously closed cup was  $113 \pm 1$  °C. The CECPRS flash point pressure profile is shown in Figure 9.

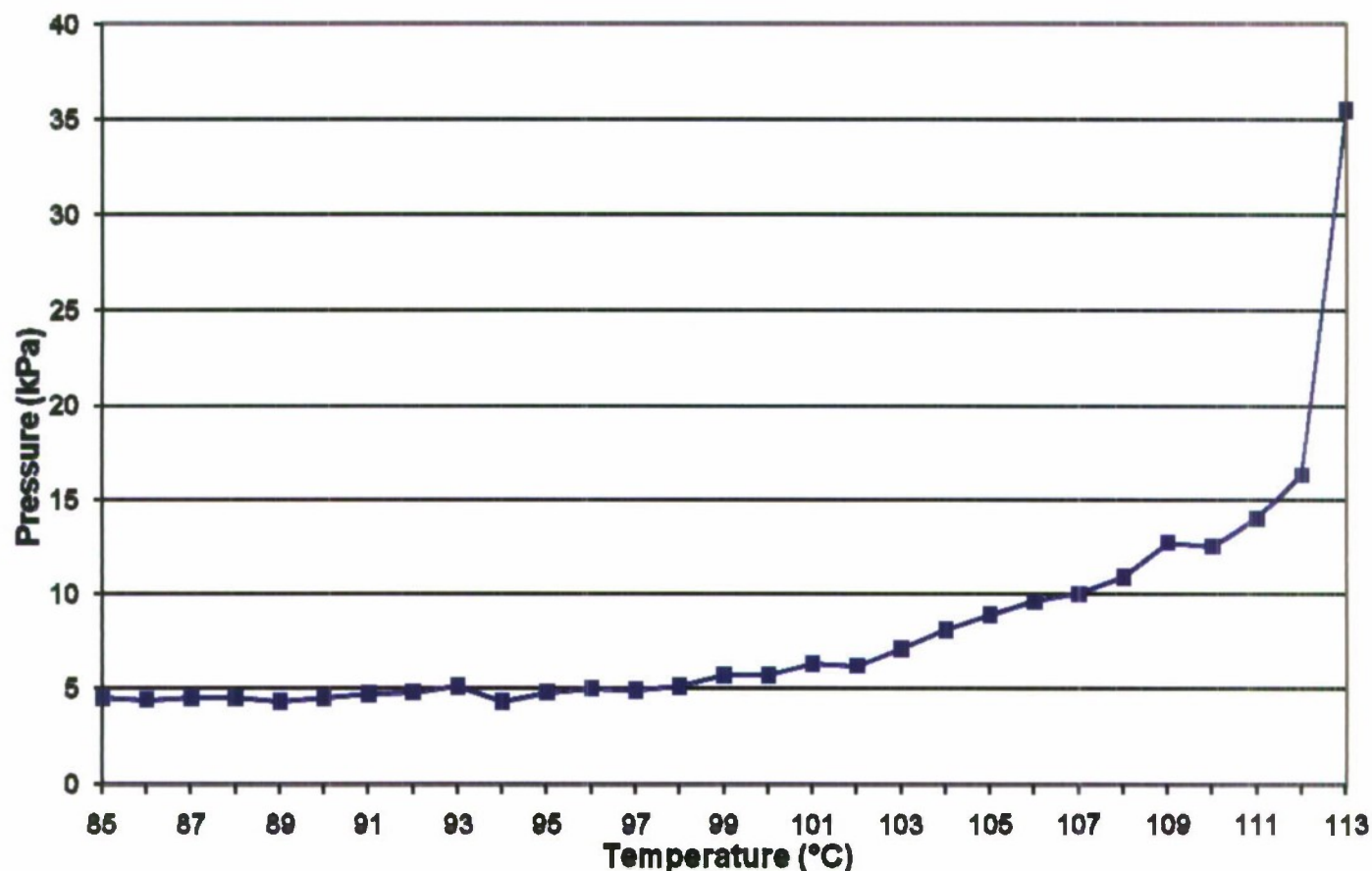


Figure 9. Flash Point Pressure Profile of CECPRS

### 3.6 Melting Point

The melting point of CECPRS was of considerable interest given the structural similarity between CECPRS and HD, which melts at 14.45 °C.<sup>23</sup> Visual inspection of the saturator cell during the -20.0 °C vapor pressure experiment indicated that the sample was a liquid.

The melting point for CECPRS was determined in duplicate and yielded a mean value of  $-63.6 \pm 0.3$  °C. A representative plot of the melting endotherm is shown in Figure 10. The smaller endotherm with an onset at approximately -49 °C is assumed to be due to an impurity in the CECPRS sample.

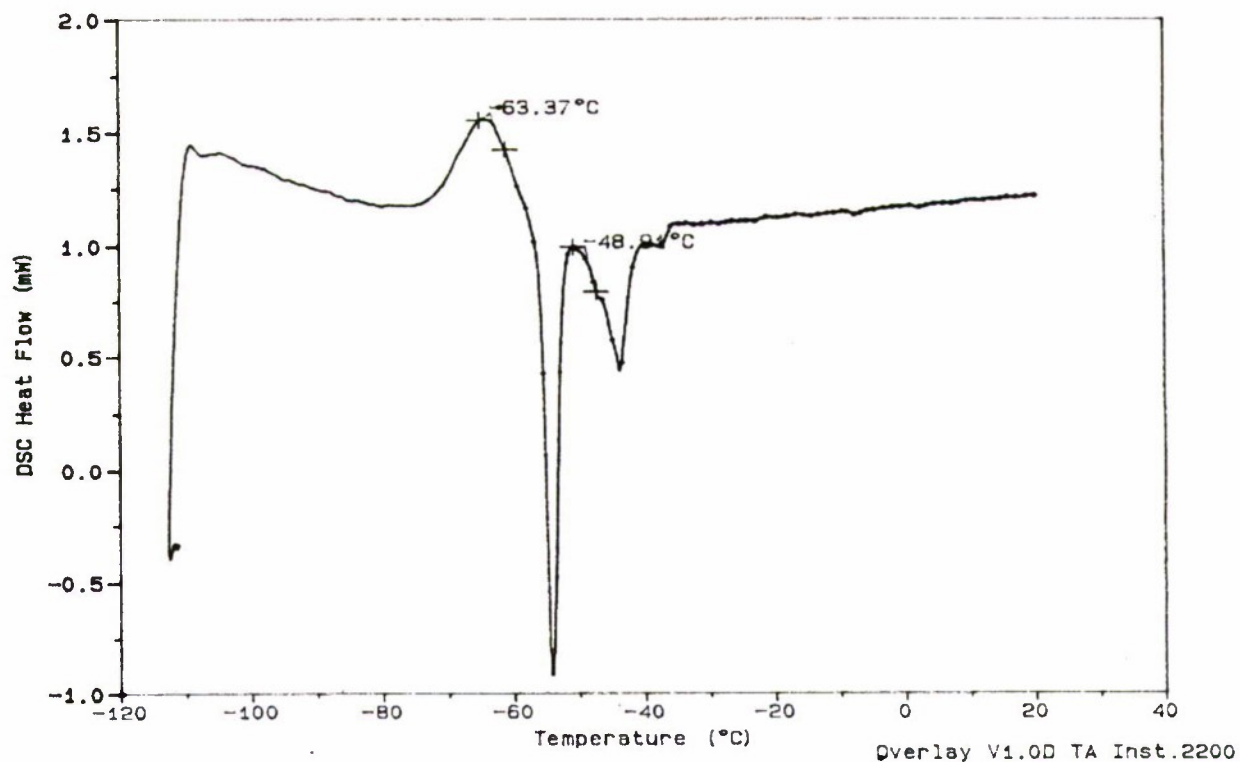


Figure 10. Melting Endotherm of CECPRS

### 3.7 Physical Properties of CECPRS and HD at 25 °C

Because CECPRS has a chemical structure similar to HD, selected physical properties of HD and the CECPRS properties documented in this report are listed in Table 8 for comparison. Although some of the CECPRS properties were determined at multiple temperatures, only the calculated values at 25 °C are shown in Table 8.

Table 8. Physical Properties of CECPRS and HD

Property	CECPRS	HD
Vapor Pressure at 25°C (torr)	$3.32 \times 10^{-2}$	$1.06 \times 10^{-1}$ (Reference 22)
Density at 25°C (g/mL)	1.21677	1.2685 (Reference 25)
Viscosity at 25°C (cSt, cP)	3.278, 3.989	3.115, 3.951 (Reference 25)
Surface Tension at 25°C (dynes/cm)	41.20	42.5 (Reference 26)
Flash Point (°C)	113 (Closed Cup)	105** (Reference 25)
Melting Point (°C)	-63.6	14.45 (Reference 23)

\*cP = centipoise

\*\*This reference does not indicate whether open or closed cup method was used.

#### 4. CONCLUSIONS

Selected physical properties were determined for 2-chloroethyl-3-chloropropyl sulfide (CECPRS), which is an impurity present in bis (2-chloroethyl sulfide) (HD) that had been stored in ton containers. These properties include: vapor pressure, density, and viscosity at multiple temperatures, surface tension at 25 °C, as well as flash point and melting point. This is the first time that all of these properties have been reported for CECPRS.

Vapor pressure data and a three-parameter Antoine correlation are provided for CECPRS. The combination of high-temperature differential scanning calorimetry DSC and ambient temperature saturator data increases the confidence in the data overall and in the ability to interpolate and extrapolate to untested conditions. It also provides insight relative to data quality.

This data will provide more accurate input to facilitate modeling efforts currently being performed in support of the Agent Fate Program.

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## APPENDIX

### METHOD FOR DETERMINATION OF THE SURFACE TENSION OF LIQUIDS USING THE WILHELMY PLATE METHOD

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Originator

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Michael W. Ellzy  
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QAC, Rsch & Tech

1. **TITLE:** DETERMINATION OF THE SURFACE TENSION OF LIQUIDS USING THE WILHELMY PLATE METHOD

1.1 **KEYWORDS:** Surface tension, Wilhelmy plate, wetted length, contact angle, platinum plate, glass cover slide.

2. **CURRENT REVISION DATE:** Rev. 0, 10 April 1998

3. **PREVIOUS REVISIONS:** None

4. **OFFICE OF CONTACT:**

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Research and Technology Directorate (R&T)  
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PHONE: (410) 671-1902/1740/2116  
FAX: (410) 671-1846

5. **APPLICATION:** This method applies to the determination of the surface tension of liquids using the Wilhelmy plate method.

5.1 **CONCENTRATION RANGE:** Samples are run as received.

5.2 **DETECTION LIMITS:** Not applicable.

5.3 **INTERFERENCES:** None anticipated at 25.0°C (ambient). Sample evaporation/condensation at temperatures significantly above/below ambient are possible.

5.4 **ANALYSIS RATE:** Up to 8 samples can be analyzed at ambient (25.0° C) in an 8-hr day, less if the desired temperature is significantly above/below ambient.

5.5 **VALIDATION:** ACS reagent grade water<sup>1</sup> was used for validation. Table 5.5 shows the precision and accuracy data which was generated for this method.



Table 5.5. Precision and Accuracy Validation Data at 25.0° C for the Surface Tension of ACS Grade Water Obtained Using Different Experimental Configurations.

Plate Description	Platinum	Glass Cover Slide	Glass Cover Slide
Vessel	Standard, 45-mL	Standard, 45-mL	Scintillation Vial
Sample Volume	30 mL	30 mL	3 mL
Surface Tension, dynes/cm.	71.78 72.02 72.08 72.03 72.19	72.00 71.78 71.73 71.61 71.75	72.34 72.16 72.37 72.32 72.10
Mean, $\bar{x}$	72.02	71.77	72.26
Standard Deviation, $\sigma_{n-1}$	0.1502	0.1419	0.1201
RSD*, %	0.2086	0.1977	0.1662
Difference from Literature <sup>2</sup> , %	+0.0417	-0.3056	+0.3751
NOTES: * RSD = Relative Standard Deviation			

6. **SCIENTIFIC BASIS:** The plate method of surface tension measurements requires the use of a small rectangle of solid, usually platinum, which is attached to a force measuring system<sup>3</sup>. The bottom edge of the plate is made to be straight and parallel to the liquid surface. The liquid is raised until it just touches the bottom edge of the plate. Force on the plate increases due to wetting of the liquid against the plate. If the contact angle between the liquid and the plate is zero, due to perfect wetting, the surface tension is easily determined.

## 7. APPARATUS:

7.1 **INSTRUMENTATION:** Krüss Processor Tensiometer K12 system or equivalent, consisting of a measuring unit and a control unit.

7.1.1 **Measuring Unit:** This consists of a force measuring system, temperature sensor, thermostatic jacket with built-in magnetic stirrer, platform drive system (to raise and lower the sample automatically and determine its position) and a guide to hold tubing from the automatic dosing system. A set of transparent doors encloses the measuring compartment to isolate it from air movements. A fluorescent light (which can be switched off) illuminates the area inside the compartment for easy positioning of sample and probes.

7.1.2 **Control Unit:** This contains interface boards to communicate with the measuring unit and to perform calculations, a printer and a liquid crystal display to present results. Two RS 232 ports allow the microprocessor to interface with an automatic dosing system and an external computer.

## 7.2 HARDWARE/GLASSWARE:

7.2.1 Wilhelmy plate, platinum.

7.2.2 Set of glass cover slides, approximately 15 mm X 15 mm, of approximate thickness 0.15 mm.

7.2.3 Digital Calipers.

7.2.4 Burner for cleaning plates (both platinum plate and glass cover slide).

## 7.3 CHEMICALS:

7.3.1 Acetone, CAS 67-64-1.

## 7.4 REAGENT SOLUTIONS: None

## 8. STANDARDS:

8.1 Water, ACS reagent grade, CAS 7732-18-5.

## 9. PROCEDURE:

9.1 **EXPERIMENTAL DESIGN:** This procedure uses the Wilhelmy plate method to determine surface tension. The plate consists of a disposable glass cover slide held in place with the manufacturer's supplied accessory. The dimensions of each cover slide are measured prior to each experiment. The default experimental configuration is shown in the last column of Table 5.5 (Scintillation vial, 3 mL sample volume).

9.2 **SAFETY CONSIDERATIONS:** Safety SOP# CR8-OSP004-96C, "Handling and Sampling of Chemical Agents".

9.3 **INSTRUMENT CALIBRATION:** The K12 system has an internal force calibration option, which is used whenever surface tension data is measured.

### 9.4 INSTRUMENT OPERATING PARAMETERS:

9.4.1 **Sensitivity:** 0.010000 g.

9.4.2 **Immersion Depth:** 1.000 mm.

9.4.3 **Time Interval:** 2 sec.

9.4.4 **Standard Deviation:** 0.02000 dynes/cm.

9.4.5 **Number of Points:** 50

9.4.6 **Fast Surface Detect:** Off

9.5 **PROCEDURE:** Commands to operate the tensiometer are given via the control unit (CU) or the external computer (CPU) (See Section 7.1.2).



9.5.1 Make sure that the thermostat bath is operating such that the desired sample temperature is set. See Appendix A, TEMPERATURE CONTROL.

9.5.2 A new cover slide is carefully measured (length, thickness) and attached to the holding accessory.

9.5.3 Place the closed scintillation vial containing at least 3 mL of sample into the vial holder. Place the vial holder into the thermostat vessel. Remove the cover from the scintillation vial.

9.5.4 Making sure that the balance is locked and the thermostat vessel is at its lower limit, carefully attach the cover slide holder to the plate suspension.

9.5.5 Unlock the balance and after making sure that the cover slide holder is freely suspended, calibrate the tensiometer using the <3> Calibration selection on the CU.

9.5.6 Allow the sample temperature to reach equilibrium IAW Appendix A.

9.5.7 Raise the thermostat vessel until the sample is a few mm below the suspended glass cover slide.

9.5.8 Set up the tensiometer to acquire data using the CPU and the parameters in Section 9.4 and then acquire data.

9.5.9 Upon completion of data acquisition, lock the balance, lower the thermostat vessel and carefully remove the cover slide holder w/the attached cover slide. Dispose of the cover slide IAW Section 9.2.

9.5.10 Replace cover on scintillation vial, remove vial holder w/vial and store sample.

9.6 CONTROL SAMPLES: NA

10. **TREATMENT OF DATA:** The CPU system generates a table of data for each experimental run. The surface tension value is extracted from this table and reported to the customer IAW ACT procedure.

11. **REFERENCES:**

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11.3 Users Manual for Processor Tensiometer K12, Krüss GmbH, Hamburg 1994.

## Appendix A - **TEMPERATURE CONTROL**

A NBS traceable thermometer is used as the reference in setting the sample temperature. The operator must physically annotate the data record for the experimental run with the correct temperature because the built-in temperature probe of the instrument does not display the correct temperature. Because there is no way to directly measure the sample temperature during the experimental run, the sample temperature settings for the bath are determined prior to the run by using a blank sample of water in the sample container. The setpoint of the circulator bath is set such that a given thermostat bath temperature equates to a desired sample temperature. Setpoints are determined for different desired sample temperatures.